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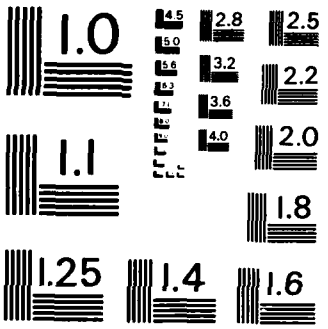

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Correlations Between Electrochemical Potentials and Optical Charge Transfer Energies in Ruthenium Bipyridine Derivatives

BY

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Linear relationships are discussed linking the Ru→π*(bpy) charge transfer transition energy in the species [Ru(bipyridine)$_2$XY]$^{n+}$ (X,Y various non-diimine ligands, n=0,1,2) and the observed potentials E[Ru(III)/Ru(II)], E[(bpy)/(bpy$^-$)] and their difference. The conditions under which such relationships might be valid are investigated. Correlation of E(Ru(III)/Ru(II)] is also explored. The results permit the use of optical energies to calculate CT energies and vice versa.

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Correlations between Electrochemical Potentials and Optical Charge Transfer Energies in Ruthenium Bipyridine Derivatives.

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There are numerous examples in the literature of correlations between charge transfer (CT) energies and specific oxidation or reduction potentials, or differences thereof [1-22]. There have been few attempts to explain the existence of the various different relationships observed. We have recently discussed how correlation of electrochemical and optical spectroscopic parameters can provide useful information not obtainable from either study alone [23,24].

In this paper we explore the correlations which exist between the observed MLCT Ru⟶bpy(π_1^*) transition (E_{op}) in $[Ru(II)(bpy)_2(XY)]^{n+}$ species (bpy = 2,2'-bipyridine, X,Y = general ligands, n=0,1,2), and E[Ru(III)/Ru(II)], $E[Ru(II)(bpy)_2/(bpy)_2^-]$ and ΔE(redox), the (positive) difference between these two quantities. E[Ru(III)/Ru(II)] is the oxidation potential of Ru(II) bound to bipyridine, and $E[Ru(II)(bpy)_2/(bpy)_2^-]$ is the first reduction potential of bipyridine bound to Ru(II).

A large body of data for $[Ru(bpy)_2XY]^{n+}$ is available in the literature though in many cases, electrochemical data are incomplete or not reported. Complexes were chosen in which:-

i) the lowest energy CT transition is clearly to bpy. All complexes with XY=diimine, other than bpy, are excluded since transitions to bpy and diimine may not be distinguishable.

ii) the relevant redox potentials are reported to be reversible (at room temperature).

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iii) the first reduction occurs at the π_1^* on bpy.

iv) the first oxidation is Ru(III)/Ru(II).

The electronic transition $Ru(II)(bpy)_2 \dashrightarrow Ru(III)(bpy)_2^-$, E_{op}, can be estimated by taking the difference between two redox potentials:

$$E_{op} = E[Ru(III)/Ru(II)] - E[Ru(III)(bpy)_2/(bpy)_2^-] + \chi_i + \chi_o \quad (1)$$

Writing:-

$$E[Ru(III)/Ru(II)] - E[Ru(III)(bpy)_2/(bpy)_2^-] = \Delta E'(redox)$$

then:-

$$E_{op} = \Delta E'(redox) + \chi_i + \chi_o \quad (2)$$

where χ_i and χ_o are the inner (vibrational) and outer (solvation) reorganisation energies of the CT excited state. Eqn.(3) has been used very successfully in discussing the LMCT spectra of metallophthalocyanines where $\Delta E'(redox)$ can be calculated and the reorganisation energies are negligibly small [25]. However, the electrochemical potential for ligand reduction bound to the oxidised metal ion is not normally available experimentally. Rather, use is made of the experimentally observable $\Delta E(redox)$, defined above, and following the development in [23], write the relationship:-

$$E_{op} = \Delta E(redox) + Q + \Delta\Delta G_s + \Delta(sol) + \chi_o + \chi_i \quad (3)$$

where, $\Delta\Delta G_s = 2\Delta G_s - \Delta G_s^+ - \Delta G_s^-$, $\Delta(sol) = \Delta G_s^* - \Delta G_s$, and Q is the free energy for transfer of an electron from the reduced to the oxidised species in the gas phase, yielding a ground state and an excited state species. The ΔG_s terms are respectively the solvation free energies of the ground state, oxidised and reduced ground state, and equilibrated excited state molecules.

Eqn.(3) is true if configurational interaction between the charge transfer state and any other states is negligible, while for eqn.(2) this assumption is unnecessary. Thus, in the absence of configurational interaction, $Q + \Delta\Delta G_s + \Delta(sol)$ represents the difference in bpy reduction potentials when bound to Ru(III) and to Ru(II). Note that the potential $E[Ru(III)(bpy)_2/(bpy)_2^-]$ refers to the singlet state. This potential for the triplet state is, however, of importance photophysically and is commonly written, for a +2 ion for example, as $E[Ru^{3+}/Ru^{2+*}]$. The singlet and triplet potentials are related by the quantity $2K + \lambda$, where K is the relevant exchange integral and λ is the spin-orbit coupling coefficient.

Several authors [14-19] have reported fairly good linear relationships between E_{op} and $\Delta E(redox)$. This suggests that eqn.(3) could be approximated by:-

$$E_{op} = \underline{a}\Delta E(redox) + const. \qquad (4)$$

where the constant collects all the solvation and reorganisation terms together, and the slope, $\underline{a}$, may be unity, but could perhaps be non-unity if any of the terms in (3) have a functional dependence upon the electrochemical potential. The scatter in such plots represents the variation in the solvation and reorganisation energies, and configurational interaction.

In Fig.1 is shown a plot of some 33 species (listed in Table 1), of $\Delta E(redox)$ versus E_{op}. The least squares line is:-

$$E_{op} = 0.86\Delta E(redox) + 0.54 \quad [eV], \text{ regression coeff. } 0.95 \qquad (5)$$

with a standard deviation between observed and calculated optical transition energies of 0.10eV. However the correlation is clearly scattered and if $\underline{a}$

constrained to be unity, the best line is then:-

$$E_{op} = 1.00\Delta E(\text{redox}) + 0.21 \quad [\text{eV}] \qquad (6)$$

with a standard deviation of 0.11eV, which is not significantly different. These equations, although they appear rather different, do, of course, predict very similar E_{op} energies for ΔE(redox) values within the experimentally observed range. Either may therefore be used to predict a transition energy where electrochemical data are available; hence they are useful for assignment purposes. Eqn.(6) agrees well with similar equations proposed by Chakravorty and co-workers [14,15], also for $[Ru(bpy)_2XY]^{n+}$ systems.

The literature also contains a number of correlations involving optical energies and one observed redox potential, most frequently that of metal oxidation in the case of MLCT transitions. Given the above equations, it is not immediately obvious why these should exist. Some authors have concluded that the energy of the acceptor orbital does not vary much for the series of compounds studied; this does not appear to be the case, in general (vide infra).

In Fig.2 is shown a correlation between E[Ru(III)/Ru(II)], vs sce, and E_{op} for some 87 complexes, listed in Table 1. The linearity is surprisingly good. The equation of the line is:-

$$E_{op} = 0.65E[Ru(III)/Ru(II)] + 2.00 \quad [\text{eV}], \text{ regression coeff. } 0.93 \qquad (7)$$

with a standard deviation between observed and calculated transition energies of 0.10eV. The correlation is especially remarkable, given the large range of E[Ru(III)/Ru(II)] potentials from -0.27 to +1.98V (vs sce). Before discussing this correlation, consider how it may be related to

eqn.(3). The existence of linear correlations (5) and (7) requires that:-

$$E[Ru(II)(bpy)_2/(bpy)_2^-] = \underline{b}E[Ru(III)/Ru(II)] + const. \quad (8)$$

A plot of these two potentials is shown in Fig.3 and has a least squares line of (33 complexes):-

$$E[Ru(II)(bpy)_2/(bpy)_2^-] = 0.22E[Ru(III)/Ru(II)] - 1.69\ [eV] \quad (9)$$

regression coeff. 0.90

Eqn.(9) may be used to estimate one redox potential, knowing the other, with a standard deviation, in the data set employed, of 0.05eV. A similar, but very limited correlation, was observed by Rillema [42].

If eqns.(7) and (9) are used to derive eqn.(5) only slightly different values of the slope and intercept (0.83, and 0.59 respectively) are obtained, giving an indication of the consistency of these relationships over a large data base.

Where substitution of various X,Y in $[Ru(bpy)_2XY]^{n+}$ leads to an increase in E[Ru(III)/Ru(II)], then $E[Ru(II)(bpy)_2/(bpy)_2^-]$ becomes less negative according to eqn.(9). Since this is a '2nd order' effect of XY, it is much smaller than the changes in E[Ru(III)/Ru(II)]. A more positive value for E[Ru(III)/Ru(II)], generated by the π-electron withdrawing nature of the XY ligands, implies an increased stabilisation of Ru(II), and an increased effective nuclear charge thereon. The extent of π-back donation to the bpy ligand must be reduced, reducing thereby the magnitude of the off-diagonal $\langle Ru(d^6) \mid r \mid bpy(\pi_1^*)\rangle$ element, and stabilising the $bpy(\pi_1^*)$ orbital [43]. Thus the $[Ru(bpy)_2]^{2+}$ chromophore is effectively acting as a probe (or spectator) of the Ru-XY interaction, as suggested previously by Meyer [34,44].

The observed E[Ru(III)/Ru(II)] potential can also be related to the second bpy/bpy$^-$ reduction process; for 30 complexes, the least square line is:-

$$E[Ru(II)(bpy)_2^-/(bpy)_2^{2-}] = 0.30E[Ru(III)/Ru(II)] - 1.99 \text{ [eV]}$$

regression coeff. 0.88

(10)

The Ru(III)/Ru(II) potential utilised in (10) is that of the un-reduced molecule, while to give the equivalent of eqn.(9) requires the comparison of the second bpy reduction potential with the Ru(III)/Ru(II) potential when Ru(II) is bound to a reduced bpy molecule. This potential is not available experimentally. However, if eqn.(9) is assumed valid, the second bpy/bpy$^-$ reduction potential can be inserted therein, and the calculated E[Ru(III)(bpy)$_2^-$)/Ru(II)(bpy)$_2^-$] potential derived. For example, with Ru(bpy)$_2$(CN)$_2$, the Ru(III)/Ru(II) potential of the Ru(bpy)$_2^-$(CN)$_2$ species would be calculated to lie at ca. -0.5V; thus oxidation of bpy$^-$ must occur prior to metal oxidation, as observed.

Discussion:

There seems no compelling experimental justification for choosing the least squares slope of 0.86 in eqn.(5) over the unit slope in (6). A slope of unity would be expected if none of the terms on the right of eqn.(3) following $\Delta E(redox)$ varied with $\Delta E(redox)$. The magnitudes of some of these parameters have been discussed previously [19,23,24]. The solvation terms, $\Delta\Delta G_s$ and $\Delta(sol)$, are differences and are independent, within the Born approximation, of the overall charge on the complex [45]. They are therefore unlikely to vary linearly with redox potential. There also seems no obvious reason why χ_1 or χ_o should so vary. Nevertheless the variation of these parameters from one species to another will cause a scatter about the best line, which represents average values. It is possible however, that Q

vary with $\Delta E(redox)$, so that the true slope is not unity. Choice of eqn(6) leads to little error.

Given a slope of unity in eq.(6), the slope in eqn.(7) (0.65) is simply a measure of the sensitivity of $E[(bpy)_2/(bpy)_2^-]$ to changes in E[Ru(III)/Ru(II)]. If Q does vary with E[Ru(III)/Ru(II)], this will also be reflected. A slope of unity in eqn.(7) would indicate that $E[(bpy)_2/(bpy)_2^-]$ was invariant with E[Ru(III)/Ru(II)], while a slope of zero would imply no change in E_{op} with redox potential. Slopes >1 would require that $E[(bpy)_2/(bpy)_2^-]$ became more negative with increasing E[Ru(III)/Ru(II)], an improbable event. Thus slopes in this kind of correlation (E_{op} vs E[Ru(III)/Ru(II)], or generally versus E(ox)), will lie between 0 and 1, and probably closer to unity than zero, depending upon the metal and ligand system.

The constant terms in eqns.(7,9,10) can be related to a grouping of parameters, once adjusted for the reference electrode used. However again the real scatter in these various parameters for different complexes means that only an average value can be obtained, and this is poorly defined.

Considering the various parameters in eqn.(3) which could cause poor agreement with Eqns.(5) (or (6)), the reorganisation energy terms are most likely to be significant. Solvatochromic species, such as $Ru(bpy)_2(CN)_2$, may obviously fit badly since they may exhibit large values of χ_o, yet within the group of species discussed here, only this dicyanide is reported as showing significant solvatochromism. The inner reorganisation energy term, χ_i, might be expected to be similar for all the complexes, since the same transition, Ru$\dashrightarrow$bpy, is involved. Significant variations in configurational interactions may also cause scatter.

There are some examples where the excited state appears to have a different equilibrium geometry from the ground state. This will be

indicated by vibrational broadening of the absorption band. For example, in figs.(1,2), points corresponding to $E_{op} > 25{,}000\ cm^{-1}$ lie clearly above the best fit line. These are compounds in which XY are phosphines or isocyanides. Chakravorty has also made a similar observation [14]. The Ru←→XY transitions are expected to lie above $30{,}000\ cm^{-1}$ so will not interfere, and there are no other allowed CT or intraligand transitions close to Ru-→bpy. However, in the phosphine complexes, the Ru-→bpy transitions are broad and skewed to higher energy [34], suggesting that the ground and excited states do indeed have different geometries. Meyer et al. [29,34] have concluded that there is extensive mixing of the Ru(d) orbitals with π-acceptor levels on the phosphine (or isocyanide), causing the ground state to be closer to Ru(III) than Ru(II), in its effective nuclear charge. PES evidence for the isocyanides also supports this explanation [29]. Since this mixing is likely to be greatly reduced in the excited state, this could explain the difference in geometry. There is also a rough correlation, in the phosphine series, between oscillator strength and E_{op}, the former increasing with the latter, in part because of the decreased π-back donation to bpy in the ground state [34].

This treatment serves three purposes. Firstly, with 'well behaved' complexes, electrochemical data may be used to assign spectra, or spectra may be used to deduce electrochemical potentials. Secondly, if a species is 'ill behaved', one is immediately alerted to some special problem in the system, and possible explanations can be deduced from the analysis shown here. Thirdly, it should eventually prove possible, with a more extensive data base and including additional experimental information such as emission and solvatochromism data, to delineate some of the terms in eqns.(2,3) more closely. The treatment is quite general and should be applicable to other series of metals and ligands, to LMCT as well as MLCT transitions, and to

emission energies [42,44], within the limitations outlined above. Preliminary analysis of $[Os(bpy)_2XY]^{n+}$ species [46] shows that similar correlations can be obtained, despite the added complexity of j-j coupling.

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Figure Legends

1. Plot of E_{op} for Ru---bpy(π_1^*) vs ΔE(redox), the difference between the Ru(III)/Ru(II) and the first bpy/bpy$^-$ redox potentials. The line for Eqn.(5) is shown.

2. Plot of E_{op} for Ru---bpy(π_1^*) vs Ru(III)/Ru(II) potentials vs sce. The line for Eqn.(7) is shown.

3. Plots of the first and second bpy/bpy$^-$ potentials vs the Ru(III)/Ru(II) potentials. * 1st bpy reduction; + 2nd bpy reduction. All potentials are vs sce. Points plotted are those for which both bpy reduction potentials are reported.

Table 1 Electrochemical and Optical Parameters for cis[$Ru(bpy)_2XY$]$^{n+}$

XY	n	Ru(III)/Ru(II) (eV)	(1) bpy/bpy$^-$ (eV)	(2) bpy/bpy$^-$ (eV)	E_{op-1} (cm^{-1})	Ref.
Hl	0	-0.27	-1.65	-1.95	13,890	14
OBzIm	0	0.09	-1.63	-1.94	17,150	26
$(N_3)_2$	0	0.17			18,020	27
$(Pz)_2$	0	0.30			17,210	28
Cl_2	0	0.32			18,080	28
$(PPh_2)_2$	0	0.32			18,150	29
H2	1	0.37	-1.62	-2.10	16,950	14
Br_2	0	0.37			18,250	30
OBzImH	1	0.39	-1.67	-2.00	18,870	26
BiBzIm	0	0.43	-1.58	-1.87	18,150	26
$(Trz)_2$	0	0.45	-1.65		18,380	31
(NCS)Cl	0	0.50			18,690	30
$(N_3)Py$	1	0.58			20,080	27
$(H_2O)_2$	2	0.63			20,830	29
$(N_3)MeCN$	1	0.65			21,100	27
$(NCS)_2$	0	0.67			19,230	30
(Pz)PzH	1	0.69	-1.50	-1.72	19,610	28
BiBzImH	1	0.72	-1.53	-1.86	19,720	26
PBzIm	1	0.72	-1.46	-1.70	20,280	26
(BPA)Cl	1	0.77			20,160	32
(Py)Cl	1	0.77	-1.50	-1.83	20,160	28
(BPE)Cl	1	0.78			20,620	32
$(Py)H_2O$	2	0.78			21,280	33

Table 1 cont--

XY	n	Ru(III)/Ru(II) (eV)	(1) bpy/bpy$^-$ (eV)	(2) bpy/bpy$^-$ (eV)	E_{op} (cm^{-1})	Ref.
(4,4'-bpy)Cl	1	0.79			20,530	32
(Bu_3P)Cl	1	0.81	-1.51	-1.76	20,620	34
(4-AcPy)Cl	1	0.82			20,200	35
$(NO_2)_2$	0	0.82			21,550	29
(Py)NCS	1	0.85			20,490	30
$(CN)_2$	0	0.85	-1.54	-1.80	21,740	36,37
(MeCN)Cl	1	0.86			20,800	35
(tBuPy)NO_3	1	0.88			20,450	30
(Pyz)Cl	1	0.88			20,830	32
(TFA)Py	1	0.89			20,040	30
(PTS)Py	1	0.90			20,330	30
(AsI)Cl	1	0.90	-1.49	-1.69	21,190	34
(Py)NO_3	1	0.91			20,490	30
($MePh_2P$)Cl	1	0.91	-1.59	-1.71	21,550	34
(P1)Cl	1	0.91	-1.51	-1.68	21,650	34
$(NH_3)_2$	2	0.92			20,410	38
(Ph_3Sb)Cl	1	0.93	-1.45	-1.61	21,280	34
(Ph_3As)Cl	1	0.93	-1.49	-1.63	21,370	34
(N-MeIm)$_2$	2	0.94			20,700	35
(P2)Cl	1	0.94	-1.53	-1.68	21,650	34
(PPh_3)Cl	1	0.94	-1.47	-1.67	22,030	34
Dach	2	0.96			20,490	38
En	2	0.96			20,620	38
Tn	2	0.98			20,330	38
Dmp	2	0.99			20,530	38
$(MeTrz)_2$	2	1.00	-1.46	-1.70	21,140	31

Table 1 cont—

XY	n	Ru(III)/Ru(II) (eV)	(1) bpy/bpy$^-$ (eV)	(2) bpy/bpy$^-$ (eV)	E_{op-1} (cm^{-1})	Ref.
$(AlTrz)_2$	2	1.01	-1.47	-1.71	21,190	31
(P3)Cl	1	1.01	-1.47	-1.65	22,680	34
$(Im)_2$	2	1.02			20,500	35
$(BuNH_2)_2$	2	1.03			20,160	39
$(Nl)_2$	2	1.04			20,330	39
$(NH_2CH_2Ph)_2$	2	1.04			20,370	39
$(PhTrz)_2$	2	1.05	-1.48	-1.70	21,370	31
$(Py)ClO_4$	1	1.09			21,100	30
AMPy	2	1.12			21,230	38
AEPy	2	1.12			21,230	38
$(HTrz)_2$	2	1.13	-1.49		21,280	31
$(PzH)_2$	2	1.18	-1.52	-1.76	21,280	28
$(tBuPy)H_2O$	2	1.18			21,460	30
$(tBuPy)_2$	2	1.23			21,550	30
$(BuNH_2)NCPr$	2	1.24			22,220	39
(Nl)N2	2	1.26			22,420	39
bpy	2	1.29	-1.33	-1.52	22,170	40
(N3)NCPh	2	1.29			22,270	39
$(Py)_2$	2	1.30	-1.32	-1.56	21,980	31
MeCN(Py)	2	1.35			22,730	30
$(3\text{-}IPy)_2$	2	1.36			22,620	35
$(Pyd)_2$	2	1.42			22,730	35
$(4\text{-}AcPy)_2$	2	1.45			22,620	35
$(Me_2PhP)_2$	2	1.45			25,250	41
$(MeCN)_2$	2	1.47			23,470	30
$(CO)(O_2CH)$	1	1.47	-1.32		24,510	16

Table 1 cont

XY	n	Ru(III)/Ru(II) (eV)	(1) bpy/bpy$^-$ (eV)	(2) bpy/bpy$^-$ (eV)	E_{op-1} (cm^{-1})	Ref.
$(NCPr)_2$	2	1.48			23,420	39
$(MePh_2P)_2$	2	1.50	-1.33	-1.53	23,420	34
$(P2)_2$	2	1.51	-1.34	-1.54	22,780	34
$(NCPh)_2$	2	1.52			24,150	39
$(N2)_2$	2	1.53			24,040	39
$(PPh_3)_2$	2	1.54			23,870	29
P1	2	1.62	-1.30	-1.50	25,380	34
Dppm	2	1.63	-1.29	-1.54	26,040	34
C_7H_8	2	1.70			23,750	29
P4	2	1.75	-1.28	-1.51	26,810	34
$(CNCH_2Ph)_2$	2	1.90			28,090	29
$(4MeOPhNC)_2$	2	1.98			28,820	29

Abbreviations:- H1, benzohydroximate; OBzImH, 2-(o-hydroxyphenyl)benzimidazole; PzH, pyrazole; H2, benzohydroxamate; $BiBzImH_2$, 2,2'-bibenzimidazole; TrzH, 1,2,4-triazole; PBzImH, 2-(2-pyridyl)benzimidazole; BPA, 1,2-bis(4-pyridyl)ethane; BPE, trans-1,2-bis(4-pyridyl)ethylene; Pyz, pyrazine; TFA, $CF_3CO_2^-$; PTS, $p\text{-}MeC_6H_4SO_3^-$; As1, $Ph_2AsCH_2AsPh_2$; P1, $Ph_2P(CH_2)_3PPh_2$; N-MeIm, N-methylimidazole; P2, $(p\text{-}MeC_6H_4)_3P$; Dach, trans-1,2-diaminocyclohexane; En, ethylenediamine; Tn, trimethylenediamine; Dmp, 1,2-diamino-2-methylpropane; MeTrz, 4-methyl-1,2,4-triazole; AlTrz, 4-allyl-1,2,4-triazole; P3, $Ph_2C{=}CPh_2$; Im, imidazole; N1, $NH_2CH_2CH{=}CH_2$; PhTrz, 4-phenyl-1,2,4-triazole; AMPy, 2-(aminomethyl)pyridine; AEPy, 2-(2'-aminoethyl)pyridine; N2, $NCCH{=}CH_2$; N3, NH_2CH_2Ph; Pyd, pyridazine; Dppm, $Ph_2PCH_2PPh_2$; C_7H_8, norbornadiene; P4, $cis\text{-}Ph_2PCH{=}CHPPh_2$. For conditions of measurement, see original references. All potentials are quoted versus sce or ssce. Note that $Ru(bpy)_2(CN)_2$ is

solvatochromic, and that other species might conceivably be so.

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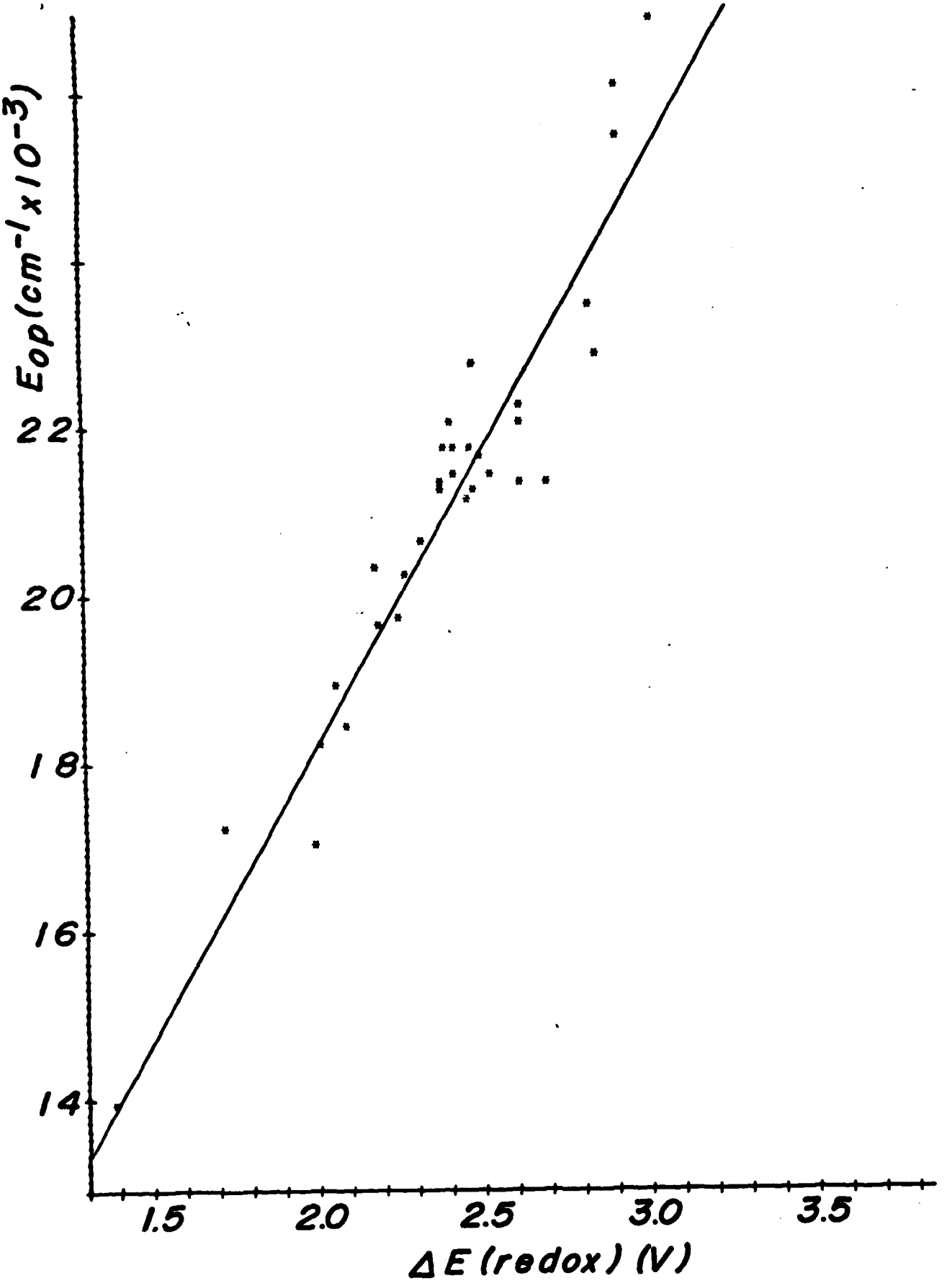
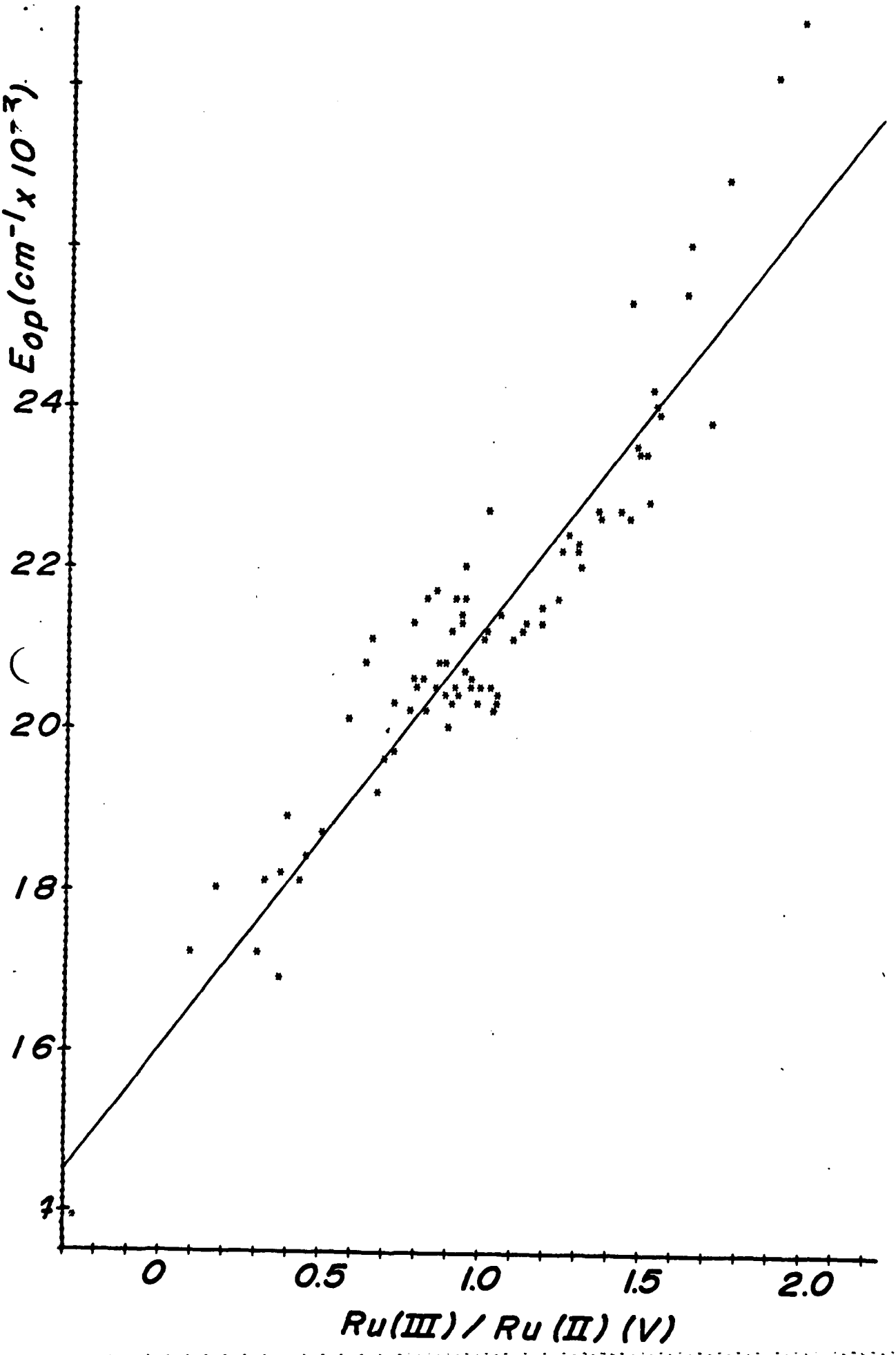


Fig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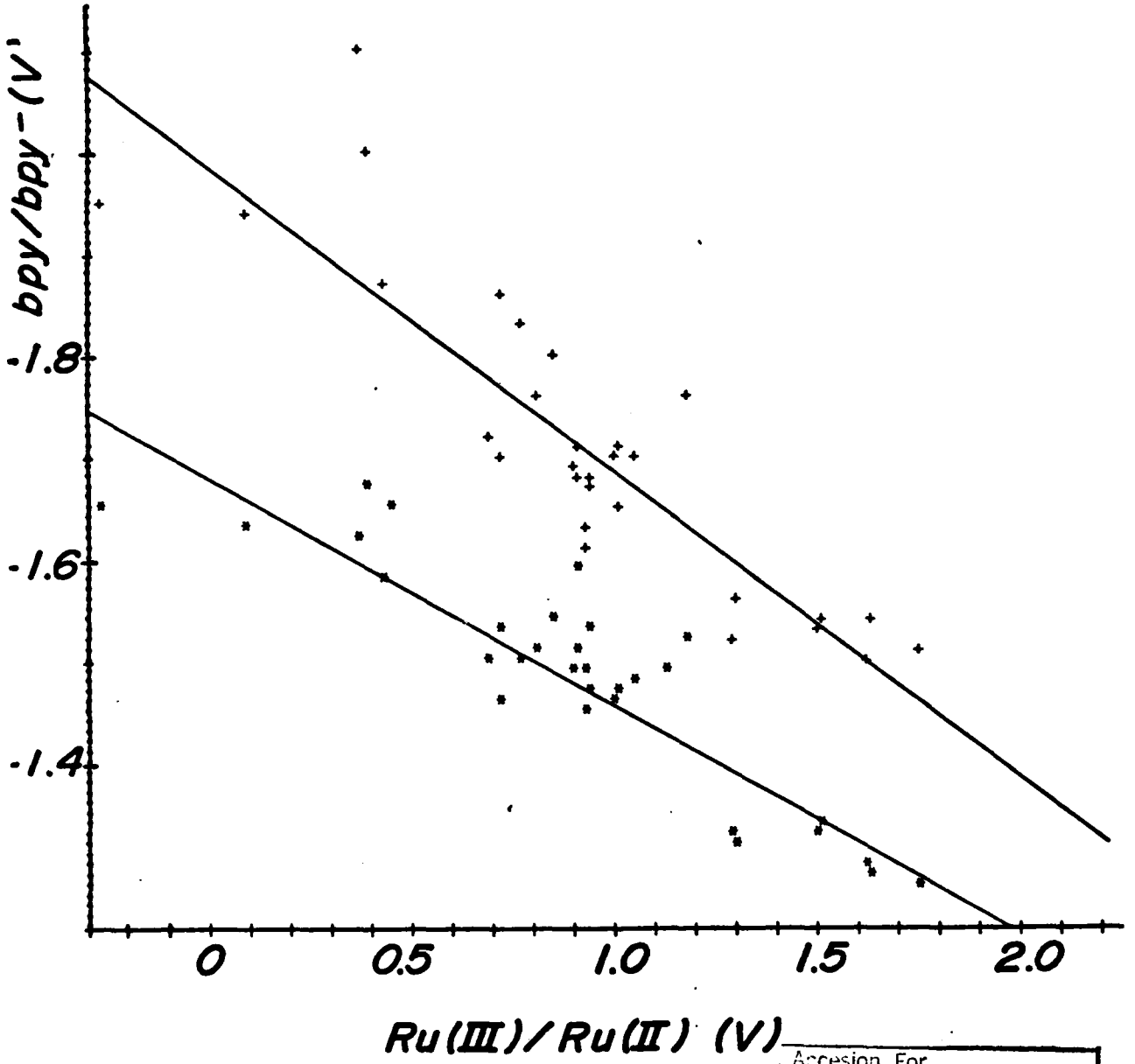

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